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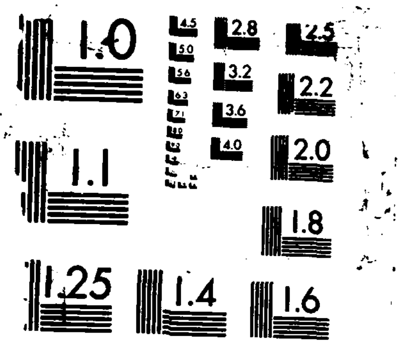
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SYNTHESIS AND STRUCTURE PROPERTY STUDIES OF TOUGHENED EPOXY RESINS VIA FUNCTIONALIZED POLYSILOXANES: FRICTION AND WEAR STUDIES

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FINAL REPORT

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This report covers the work done in the Mechanical Engineering department on the friction and wear of the siloxane modified epoxies from 1 May 1986 to 30 September 1986. This period represented an no cost time extension which was granted by ONR for the purpose of concluding these experiments.

INTRODUCTION

The friction and wear properties of copolymers of dimethyl (DM) and methyl trifluoropropyl (TFP) siloxane and of ATBN and CTBN rubber modified epoxies were previously reported [1]. There was no significant evidence that the low surface energy siloxane-modified epoxies reduced friction compared with the unmodified epoxy or the ATBN and CTBN modified epoxies. The reduction in wear noted for increasing amounts of siloxane or rubber in the epoxy was attributed to the lower surface stresses cause by the reduction in elastic modulus. The dependence of the time to initiate a wear track in the ball-on-epoxy disk experiment on elastic modulus was different for the siloxane and rubber modified epoxies. As the modulus decreased initiation times decreased for the siloxane modified epoxies while the reverse was true for the rubber modified epoxies.

In the continuation of this work the friction and wear of the copolymers of dimethyl and diphenyl (DP) siloxane modified epoxies were measured. In addition, an abrasive wear experiment was performed to determine if the wear rates varied as the inverse of the energy to rupture of the materials [2]. Another experiment was performed in which the wear debris produced was blown out of the wear track to test the hypothesis that the wear debris changed the predominant wear mechanism from fatigue to abrasive and thus caused a higher wear rate. The experiments and the results are described in this report.

EXPERIMENTAL

The preparation of the materials is described in [1]. Two different ratios of DP and DM monomers were chemically incorporated into the epoxy resin (1:4,2:3). The former ratio will be called 20 percent and the latter 40 percent. These modified epoxies were then added to epoxy resin in the amounts of 5, 10, and 15 percent by weight before curing. The seven different compositions were designated by two numbers; the first is the percent of the siloxane modified epoxy in the epoxy resin and the second is the percent DP in the siloxane copolymer. For example, 0-0 is the epoxy control sample.

For tensile tests standard dog-bone samples (cf. ASTM D638) were machined from 3x50x50 mm cast plates. The samples were pulled at a crosshead speed of 5 mm/min. Fracture toughness and flexural modulus were determined in a three-point bending apparatus. The flexural samples measured 1.7x13.4x52 mm and were placed in the apparatus which had a span of 25.4 mm. The crosshead speed for fracture toughness was 0.5 mm/min and for flexural modulus 1.0 mm/min.

Two types of wear experiments were performed on a pin-on-disk machine. In the first, a chromium steel sphere was the pin and the modified epoxy cast plate was the disk. The test conditions were: normal load - 10 N, sliding speed - 0.63 m/s, temperature - 24 C, and relative humidity - 40 to 70 percent. In the exper-

iments to observe the effects of wear debris, a nozzle directed high velocity air at the wear track to blow the debris particles out of the track before they could interact with the steel pin. Wear was characterized by the cross sectional area of the wear groove which was measured by a contacting stylus profile meter. In all tests the wear track cross sectional area was measured every 2 kc of disk rotation for 14 kc after the wear track formed. The slope of the linear regression of the wear track cross sectional area versus cycles of disk rotation was the wear rate.

In the second test, modified epoxies were cast into cylindrical pins 4.7 mm dia. which were loaded against 320 grit abrasive paper which was glued to a rotating steel disk. The test conditions were: normal load - 5 N, sliding speed - 0.27 m/s, and the temperature and relative humidity were the same as in the first test. The pin was weighed every 50 cycles of disk rotation and the wear rate was expressed as the mass lost per cycle of rotation.

RESULTS

The average mechanical properties calculated from the tensile tests are given in Table 1. With the exception of the 10-20 sample increasing siloxane content decreased the elastic modulus and the decrease was more for the 40 percent DP. Except for sample 15-40, the siloxane modified epoxies had greater elongation to rupture than the control and the elongation decreased as the siloxane content increased. The product of the elongation and the stress at rupture is an approximation of the energy to fracture. The fracture and flexural properties are given in Table 2. With the exception of sample 10-20 the plain strain stress intensity factor increases with increasing siloxane content. The strain energy also increases with increasing siloxane content and the increase is more for the 40 percent DP.

The average number of cycles to initiate a wear track and the average wear rates with and without the debris left in the wear track are given in Table 3. With the exception of sample 10-20, an increase in siloxane content resulted in a decrease in the wear rate. For the 40 percent DP the effect of removing the debris on the wear rate was dependent on the amount of siloxane in the epoxy. At 5 percent there was no difference; at 10 and 15 percent removing the debris increased the wear rate.

The coefficient of friction before the initiation of the wear track was .12 to .13 for the 5-20, 10-20, and 15-20 samples. For the 40 percent DP samples the friction coefficient increased with increasing siloxane content, .13 at 5 percent, .17 at 10 percent, and .21 at 15 percent. The coefficient of friction rose after the wear track initiated and was lowest for the 15-20 and 15-40 samples with values between .20 and .25. The coefficient of friction was higher when the debris was removed.

Only two samples were tested for abrasive wear, 5-40 and

TABLE 1

Average Mechanical Properties

Sample	Elong. (%)	S_{ult} (MPa)	S*Elong. (MPa)	Modulus (MPa)
control	**15**	**61**	**9.2**	**490**
5-20%	19	58	11.1	451
10-20%	18	66	11.6	509
15-20%	18	55	9.7	454
5-40%	18	64	11.6	477
10-40%	17	58	9.8	456
15-40%	15	51	7.8	437

TABLE 2

Fracture Results

Sample	E_f (GPa)	K_{IC} ($x10^{-6}NM/^{3/2}$)	G_{IC} (J/M^2)
control	**2.0**	**0.77**	**296**
5-20%	--	0.82	--
10-20%	1.9	0.87	398
15-20%	1.44	0.83	478
5-40%	1.9	0.91	436
10-40%	1.73	0.93	500
15-40%	1.83	1.34	981

E_f Flexural Modulus

K_{IC} Plane-strain Stress Intensity Factor

G_{IC} Strain Energy (Fracture Toughness)

TABLE 3

Wear Results

Sample	Init. (kc)	Wear Rate $x10^{-6} CM^2/KC$	Wear Rate w/o debris
control	--	**8.0**	--
5-20%	2.0	7.3 (6.0-8.5)*	--
10-20%	1.0	11.8 (9.5-14)	--
15-20%	6.7	2.2 (1.2-3.2)	--
5-40%	0.78	11.2 (7-15.5)	11.5(-)
10-40%	7.54	8.5 (4.4-12.5)	15 (13-17)
15-40%	2.4	2.4 (1.6-3.2)	9.35 (8-10.7)

* Mean values and 95% confidence limits.

15-40. The 15-40 had a wear rate of 0.102 mg/cycle while the wear rate for the 5-40 sample was .135 mg/cycle.

DISCUSSION

In previous tests [1] with DM and DM-TFP copolymers the wear rate decreased as the percent siloxane increased. At 5 percent DM siloxane the wear rate was higher than the control. The results in Table 3 show that the wear rate drops as the siloxane content increases except for sample 10-20. Table 2 shows that sample 10-20 has the highest modulus. Previous results and these results show a positive correlation between elastic modulus and wear rate but the scatter is very large. As noted in [1] the fatigue theory of wear predicts that wear rate and elastic modulus are positively correlated. The reason is that a higher modulus causes the stresses in the contact to be higher. Higher cyclic stresses cause failure in a fewer number of cycles which results in more wear particles formed in a given number of stress cycles.

One of the anomalies of this and previous data is that the wear rate is higher for the 5 percent siloxane samples than it is for the control, but their elastic moduli are lower. The CTBN samples from the previous work also had higher wear rates at the 5 percent level. It seems that 10 percent is required before a reduction in wear occurs.

The 40 percent DP samples show almost linear relationships between wear rate and both modulus (positive slope) and fracture toughness (negative slope). However, neither of the relationships can be extrapolated to the data for the control sample. In both cases the control sample has less wear than would be predicted by the linear relationship.

It was hypothesized that the wear debris from the wear track could be dragged along by the slider and loosen additional wear particles. Thus the wear after the track formed would be a combination of fatigue and abrasive wear. To test this hypothesis the wear debris was blown out of the wear track. The data in Table 3 shows that at 10 and 15 percent siloxane, the removal of the debris **increased** the wear rate. Thus the debris at the higher siloxane percentages helps to decrease the wear. One explanation for this result is that the debris rather than being abrasive may be rubbery. If so then the debris could be rolling along under the ball. The difference between the debris-no debris tests is only significant at the higher siloxane contents at which the sources for siloxane debris are more plentiful. The friction data also can be explained by rubbery debris. Lower friction with debris present could also be explained by rubbery rolls of debris in the interface.

The limited abrasive wear test show that the wear rate decreases as both the fracture toughness and stress intensity factor increase. This result is in agreement with data from other investigators [2] which showed that wear rate correlated with the inverse of the energy to rupture.

The reduction in wear by the modification of epoxies with siloxanes depends on the amount of the modifier and the size distribution of the domains produced during curing. The domains in the samples used in this study were quite variable. Some samples had domains all of approximately the same size and evenly distributed while others of the same composition had an extremely large range of sizes quite non uniformly distributed. The wear characteristics of such samples would usually be quite different. It is clear that further studies on the factors which control the size distribution of the domains is required so that domain size distributions can be consistently produced.

CONCLUSIONS

The dimethyl-diphenyl copolymer modifiers reduce wear rates at 10 and 15 percent compositions. This result is the same as previously found for dimethyl, dimethyl-trifluoropropyl, ATBN, and CTBN modified epoxies. However, these results are dependent on the domain size distribution in the matrix.

At 10 and 15 percent compositions of 40 percent diphenyl the removal of the wear debris increases the wear rate. It is presumed that the wear debris is more rubbery than abrasive and that the debris tends to roll rather that slide in the interface.

The abrasive wear of the 40 percent diphenyl samples is less at the higher (15 percent) level. This result correlates positively with the inverse of both the stress intensity factor and fracture toughness.

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